# *Ab Inito* Studies into the Role of Water on the Energetics of Organophosphate Surface Adsorption

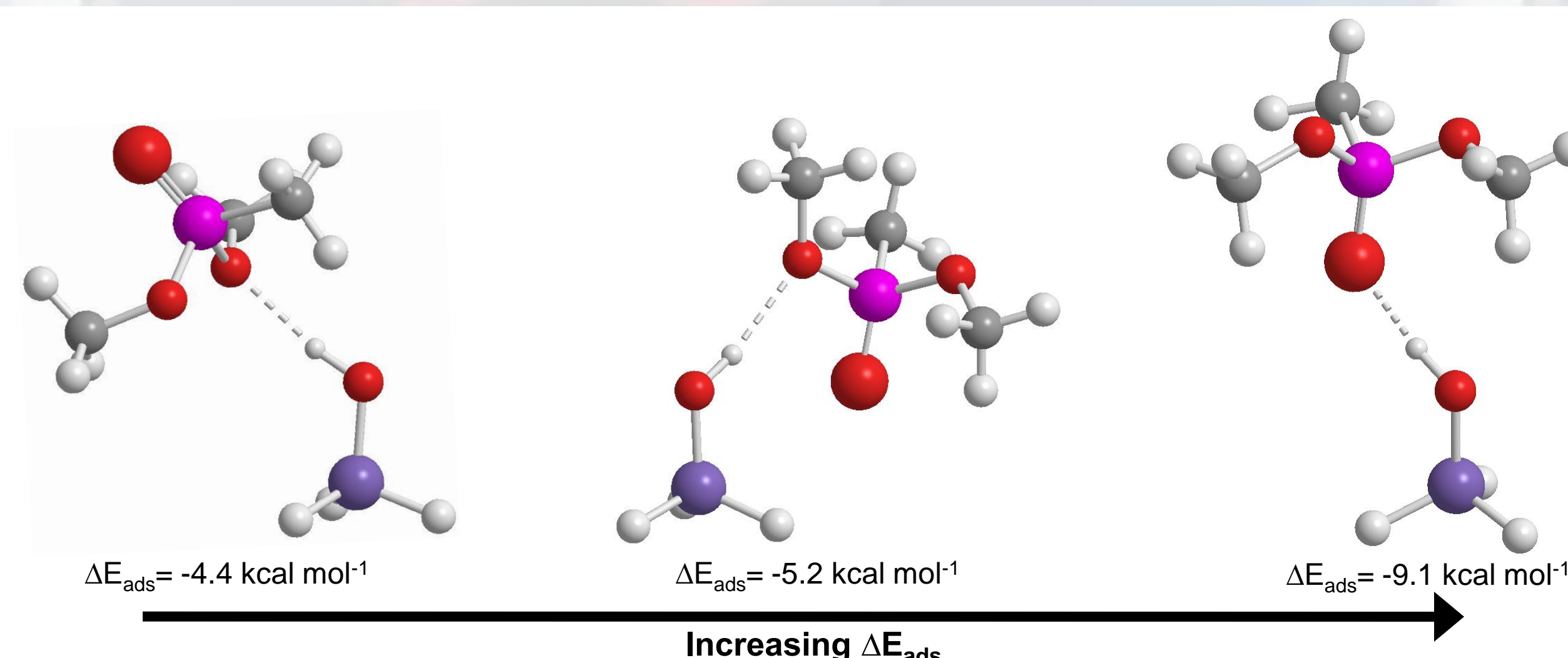Janelle E. Jenkins[1], Charles J. Pearce[2], Catherine F. M. Clewett[3], Amy Garner[1], Todd M. Alam[1]

[1]Department of Electronic and Nanostructured Materials, Sandia National Laboratories, Albuquerque, NM 87185

[2]Fort Hays State University, Hays, KS 67601, [3]West Texas A&M University, Canyon, TX 79016

The interaction of chemical warfare agents (CWA) with surfaces are being investigated in the hopes of developing better materials and coatings that are CWA resistant. Water has been observed to change the interactions of nerve agents or organophosphate (OP) agents with surfaces and in some cases has been shown to accelerate decomposition. Elucidating the role that water plays in the interaction between OP and surfaces will be important in understanding the decomposition and lifetimes of CWA in the environment. Further knowledge of decomposition may assist in the development of decontamination processes for protective clothing and detection equipment, as well as treatment and decontamination of affected environmental sites.

Due to the extreme hazards associated with CWA, computational methods are being utilized to study the interaction of CWA with surfaces. However, past computational studies investigating the interactions between OP and surfaces have neglected water that is present in any real world exposure to CWA. We have performed tandem *ab inito* calculations for Sarin and the simulant DMMP (dimethyl methylphosphonate) to study the adsorption energy of each molecule on model $SiO_2$ surfaces in the presence of water. Adsorption energies will be presented for Sarin and DMMP on the $H_3SiOH$ and $H_7Si_8O_{12}OH$ clusters in the presence of 1, 2, and 3 explicit waters. The differences in energies of adsorption between water displaced from the surface during OP adsorption and water displaced from an OP-water cluster during adsorption onto a surface will be evaluated and discussed. These results are compared to adsorption energies for Sarin and DMMP in the absence of water. In addition to adsorption energies, the geometry of adsorption is also investigated and the lowest energy geometry presented. [31]P nuclear magnetic resonance (NMR) chemical shifts and IR frequencies have been calculated for the lowest energy adsorption geometries of Sarin and DMMP on these two surfaces in the presence of water. The effect that the number of explicit waters has on the chemical shifts and adsorption energies for adsorbed Sarin and DMMP will be discussed. In addition to formulating a better understanding of the role that water plays in the adsorption of OP on surfaces, the correlations made between the calculated ^{31}P chemical shifts and adsorption geometries are a step forward towards establishing a method for determining binding geometries that can be used for comparison to future experimental data of DMMP adsorption to $SiO_2$ surfaces in the presence of water.

## DMMP Conformers Adsorbed to Model SiOH Surfaces



$\Delta E_{ads}$= -4.4 kcal mol^{-1}     $\Delta E_{ads}$= -5.2 kcal mol^{-1}     $\Delta E_{ads}$= -9.1 kcal mol^{-1}

**Increasing $\Delta E_{ads}$**

### Adsorption of DMMP on $H_3SiOH$

| Conformer | Adsorption Site | $\Delta E_{abs}$* kcal mol^{-1} | [31]P Shielding (ppm) |
|---|---|---|---|
| A | O=P | -9.1 | -260.0 |
| C | OCH₃ | -5.2 | -265.9 |
| A | OCH₃ | -4.4 | -260.3 |

### Adsorption of DMMP on $H_7Si_8O_{12}OH$

| Conformer | Adsorption Site | $\Delta E_{abs}$* kcal mol^{-1} | [31]P Shielding (ppm) |
|---|---|---|---|
| A | O=P | -10.4 | -257.9 |
| C | OCH₃ | -5.8 | -266.4 |
| A | OCH₃ | -4.8 | -261.6 |

*Energies obtained at B3LYP 6-311++G(2d,2p)

• Multiple conformers and adsorption sites are observed for DMMP on both surfaces. However, the most prevalent from a sampling of 50 runs is conformer A, the lowest energy conformer, adsorbed at the P=O to the OH of the surface.

• The magnitude of $\Delta E_{abs}$ for DMMP adsorbed on the two surfaces is determined by the binding site, not by the size of the surface.



$\Delta E_{ads}$= -4.8 kcal mol^{-1}     $\Delta E_{ads}$= -5.8 kcal mol^{-1}     $\Delta E_{ads}$= -10.4 kcal mol^{-1}

**Increasing $\Delta E_{ads}$**
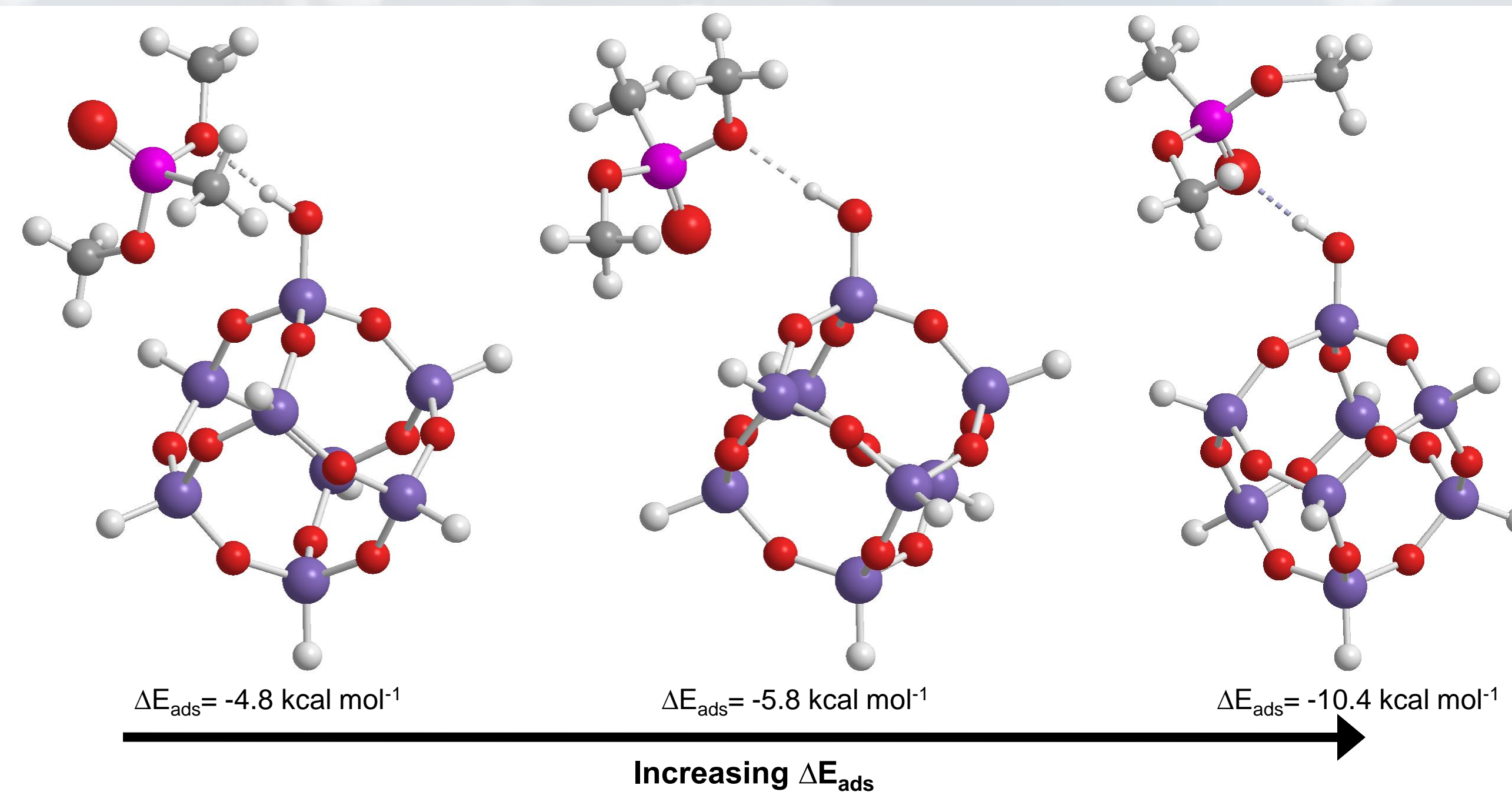
## Adsorption of Explicit Waters on Model Surfaces



|  | $H_3SiOH$ | $H_7Si_8O_{12}OH$ |
|---|---|---|
| # H2O | $\Delta E_{abs}$* kcal mol^{-1} | $\Delta E_{abs}$* kcal mol^{-1} |
| 1 | -5.7 | -6.5 |
| 2 | -15.1 | -15.8 |
| 3 | -27.0 | -27.4 |

*Energies obtained at B3LYP 6-311++G(2d,2p)

• Two surfaces were used to determine the impact of surface size on the $\Delta E_{abs}$ of water on the surface

• $\Delta E_{abs}$ is larger for $H_7Si_8O_{12}OH$, but not significantly indicating that surface size may not have a large impact on $\Delta E_{abs}$

• The more significant result is the large $\Delta E_{abs}$ for 3 waters on both surfaces, ~27 kcal mol^{-1}. This indicates that if water is present on the surface, it is unlikely that DMMP or Sarin will energetically be able to displace the water.
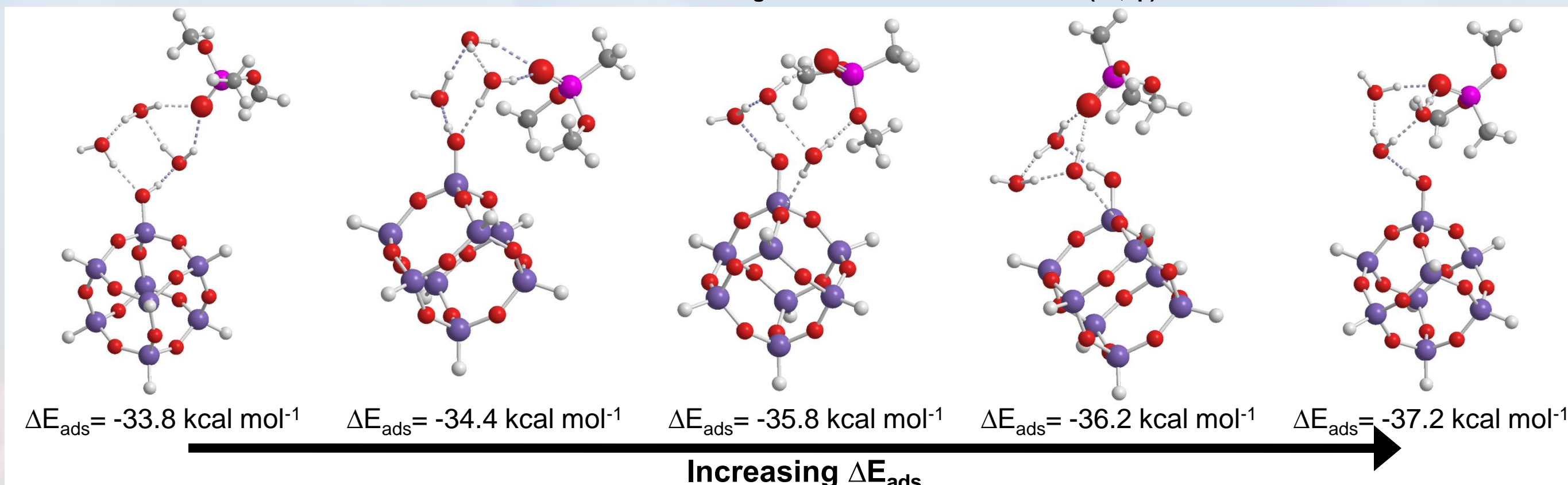


$$\delta^{deformation}$$
$$\delta^{deformation} + \delta^{HB}$$
$$\delta^{deformation}$$
$$\Delta E_{abs}$$

$\delta^{deformation}$ = deformation energy

$\delta^{HB}$ = hydrogen bonding energy
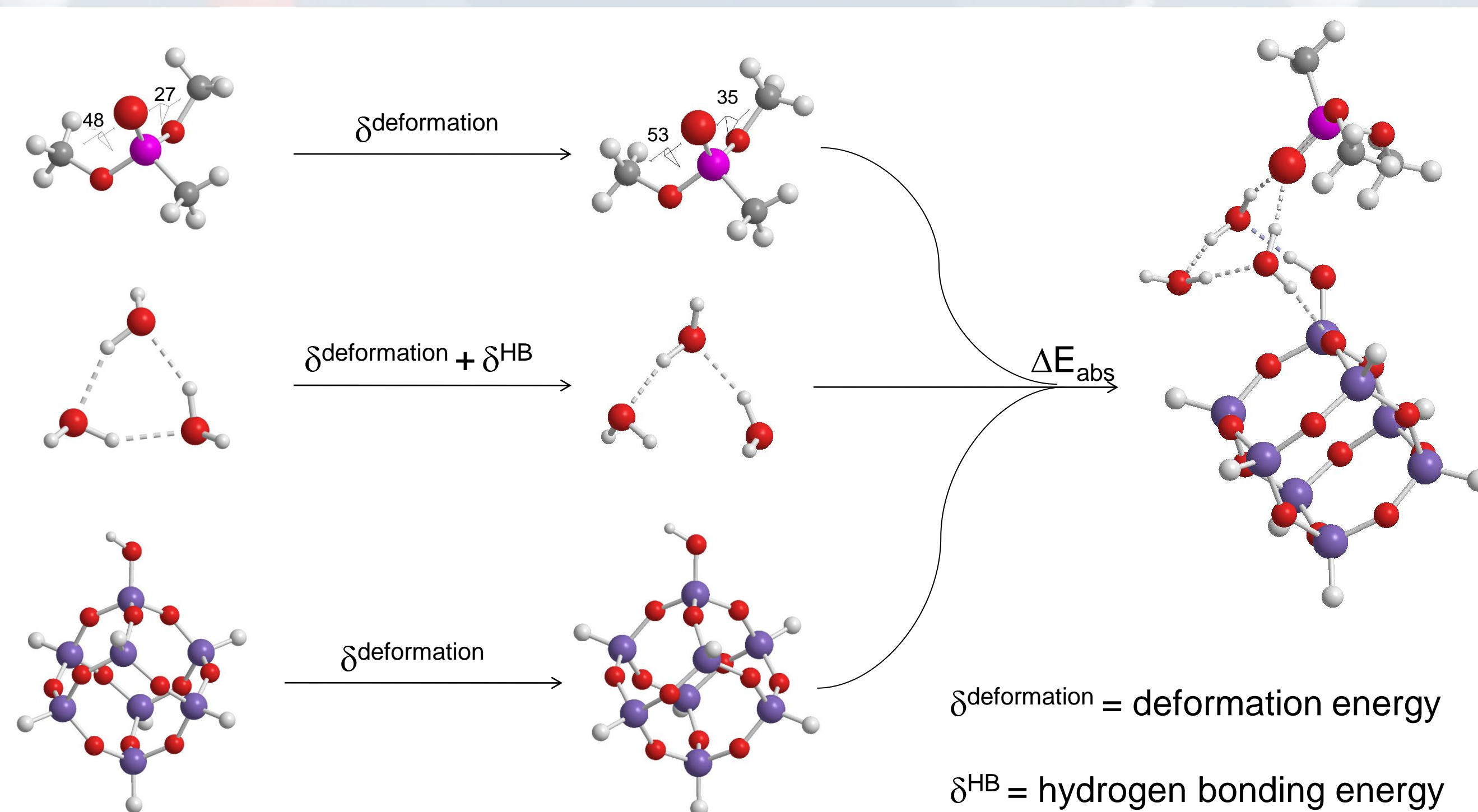
## Adsorption of DMMP on $H_7Si_8O_{12}OH$ with 3 Explicit Waters

| Conformer | Surface $\delta^{deformation*}$ kcal mol^{-1} | DMMP $\delta^{deformation*}$ kcal mol^{-1} | Water $\delta^{deformation*}$ kcal mol^{-1} | Water $\delta^{HB*}$ kcal mol^{-1} | $\Delta E_{abs}$* kcal mol^{-1} | [31]P Shielding (ppm) |
|---|---|---|---|---|---|---|
| A | 1.3 | 1.6 | 0.6 | 3.9 | -37.2 | 250.7 |
| A | 1.8 | 0.7 | 0.6 | 9.1 | -36.2 | 258.2 |
| C | 1.3 | 3.1 | 1.1 | 9.7 | -35.8 | 263.4 |
| A | 0.8 | 0.9 | 1.1 | 8.2 | -34.4 | 258.8 |
| A | 1.1 | 0.7 | 0.7 | 8.8 | -33.8 | 258.8 |

*Energies obtained at B3LYP 6-311++G(2d,2p)

• With the addition of explicit waters, the dihedral angles that define the DMMP conformer have increasing variability within a specific conformer. This can be seen in the different $\delta^{deformation}$ for DMMP.



$\Delta E_{ads}$= -33.8 kcal mol^{-1}   $\Delta E_{ads}$= -34.4 kcal mol^{-1}   $\Delta E_{ads}$= -35.8 kcal mol^{-1}   $\Delta E_{ads}$= -36.2 kcal mol^{-1}   $\Delta E_{ads}$= -37.2 kcal mol^{-1}

**Increasing $\Delta E_{ads}$**

## Sarin Adsorption on $H_3SiOH$ in the Presence of Explicit Water

| # H2O | $\Delta E_{abs}$* kcal mol^{-1} | [31]P Shielding (ppm) |
|---|---|---|
| 1 | -16.8 | -254.9 |
| 2 | -24.8 | -256.9 |
| 3 | -34.2 | -256.2 |

*Energies obtained at B3LYP 6-311++G(2d,2p)

## DMMP Adsorption on $H_3SiOH$ in the Presence of Explicit Water

| # H2O | $\Delta E_{abs}$* kcal mol^{-1} | [31]P Shielding (ppm) |
|---|---|---|
| 1 | -17.9 | -254.7 |
| 2 | -26.0 | -257.1 |
| 3 | -35.3 | -258.4 |

*Energies obtained at B3LYP 6-311++G(2d,2p)



• In both cases for Sarin and DMMP the $\Delta E_{abs}$ increase similarly with the addition of water. When increasing from 1 to 2 explicit waters there is ~8 kcal mol^{-1} difference. With an additional water, there is an increase of ~9.4 kcal mol^{-1} between 2 and three explicit water.

## Conclusions

• The $\Delta E_{abs}$ of DMMP to a surface is significant at -9 to -10 kcal mol^{-1} compared to the $\Delta E_{abs}$ of 1 explicit water on a surface (~ 6 kcal mol^{-1}). However at 2 explicit waters, the $\Delta E_{abs}$ dramatically increases to ~15 kcal mol^{-1}. This indicates that in the presence of water, DMMP will not be able to directly adsorb to the surface. This is predominately what has been observed in these current simulations. In the presence of water, both DMMP and Sarin will form a hydrogen bonded network between the water and the surface, but will not directly adsorb to the surface

• Further calculations are needed to determine a significant trend for the ^{31}P chemical shift. Although changes are observed for various conformers and adsorption sites/orientations, no definitive conclusions can be made at this time to develop a method for utilizing ^{31}P chemical shifts as an experimental method for studying these interactions.

• Although the $\Delta E_{abs}$ for Sarin and DMMP on a surface in the presence of water do differ, with DMMP being a little higher, the $\Delta E_{abs}$ do trend, indicating that DMMP in the presence of water can be used as a simulant for Sarin.

## Work In Progress

• Continue further simulations of the adsorption of Sarin on ideal surfaces in the presence of water to confirm trends observed in DMMP.

• Expand simulations to larger amorphous SiOH surfaces. These surfaces have more adsorption sites and will provide details that are closer to real world interactions.

• Compile IR and NMR data to determine trends that may be used experimentally characterize and follow these interactions.